PATENT SPECIFICATION (11) 1208521

1208521

NO DRAWINGS

(21) Application No. 48823/68 (22) Filed 15 Oct. 1968
(31) Convention Application No. 844 (32) Filed 10 Jan. 1968 in
(33) Japan (JA)
(45) Complete Specification published 14 Oct. 1970
(51) International Classification A 23 c 7/00; C 02 b 1/32; C 13 d 3/12; G 21 f 9/00
(52) Index at acceptance
A2E 1
G6R 1A10 1B1

(54) IMPROVEMENTS IN OR RELATING TO DECONTAMINATION OF MATERIALS

(71) I, TSUTOMU KUDO, a Citizen of Japan, of No. 43—310 Yurigaoka-danchi, 2—5 Yurigaoka Kawasaki-city, Kanagawa Prefecture, Japan, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of removing radioactive contaminents.

More particularly, the present invention relates to a method of removing radioactive contaminants from materials, especially dairy products, food stuffs, drinking water, or from water used in the food industry.

The use of radioactive materials is a fact of modern life, and there is constant danger that radioactive substances will contaminate foodstuffs, drinking water and water used in processing foodstuffs and then, in turn, be incorporated in the human body. Namely, as the result of nuclear bomb tests, radioactive fission products have been detected in drinking water, water used in processing foods, dairy products, and in other foodstuffs, and it is desirable to remove these radioactive contaminants.

The radioactive substance considered most dangerous for human beings is strontium-90 which has a half-life of 27 years and an effective half-life of 18 years. Strontium is similar to calcium in chemical behavior and, like calcium, is deposited in and accumulates in bone tissue. Other radioactive substances produced from a nuclear fission include strontium-89, iodine-131, cesium-137, etc. Strontium-89 and iodine-131 have short half-life periods, i.e. 51 days and 8 days, respectively, and, therefore, are not considered to be highly dangerous for the human body unless taken in large quantity. The half-life of cesium-137 is 30 years, but its effective half-life is short, i.e. 138 days, and, therefore, cesium-137 is not dangerous in comparison with strontium-90 since cesium-137 is dispersed throughout the body and is readily excreted even if it is taken into the body. At present, the influence of trace amounts of radioactive substance on the human body has not yet fully been clarified. However, it is considered desirable to prevent them from entering the human body.

Since the nuclear experiments at Bikini Atoll, various methods of removing radioactive substances from drinking water, water used in processing foodstuffs, and liquid foodstuffs, in particular cow's milk, have been examined intensively, and developed. The decontaminating methods which have been developed up to now include an ion exchange method, electrodialysis, and an adsorption centrifugation method. These methods are all applicable to removing radioactive contaminants from liquid foodstuffs, drinking water and water used in processing foods. However, when used on an industrial scale, all these methods have various defects. Cow's milk, for example, is so complex in composition that it is very difficult to remove radioactive components from cow's milk in a commercial operation. When these well known methods are used to remove radioactive contaminants from cow's milk, various disadvantages result, as noted below.

The main disadvantage of the ion exchange method is that the ion exchange resin loses its exchanging ability. After a given quantity of cow's milk has passed through, the resin must be chemically regenerated for reuse, and, therefore, it is impossible to carry out a continuous decontamination operation. Further, the regeneration of exchanger resin requires a great deal of time, expense and labor, and, in order to perform decontamination effectively, it is necessary to reduce the pH of the cow's milk with citric acid to approximately 5.3 before passing through the resin and thereafter to return the pH to the normal acidity of cow's milk with potassium hydroxide or the like. The other disadvant-

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ages of this method are that the new additional equipments are needed to be supplemented to the conventional milk processing equipment and, also, the adsorption capacity per unit time is too small for commercial purposes.

Electrodialysis has advantages over the ion exchange resin adsorption in that it does not require regeneration and continuous operation is possible. However, with electrodialysis, too, if decontamination is to proceed at a satisfactory rate, it is necessary to adjust the pH of the cow's milk with citric acid to from 5.2 to 5.4 and, after dialysis, to readjust the pH to normal value of cow's milk. Further, proteins are readily precipitated and lost. Another disadvantage is that permeability of a cation exchange membrane is not good with respect to divalent ions and, therefore, to achieve a satisfactory operating capacity with respect to unit time, large equipment is needed to carry out electrodialysis on a commercial scale.

The adsorption centrifugation method takes advantage of the fact that a radioactive substance is adsorbed in an added adsorbent. In this method a calcium salt, such as calcium phosphate, calcium carbonate, calcium lactate, and the like, or a magnesium salt is added to cow's milk and, after stirring, the resulting precipitate is separated by means of centrifugation. However, L. F. Edmondson (Journal of Dairy Science, *48*, 1597, (1965) listed the main defects of this method as follows:

1. The loss of important components in treated cow's milk treated with the above mentioned calcium salts is serious, amounting to 20 to 30% of the nitrogen, 15 to 73% of the calcium and 46 to 48% of the phosphorus.
2. The milk is made unpalatable due to the unpleasant taste imparted.
3. A large quantity of the calcium salt is required.

As pointed out above, although the rate of decontamination by the conventional decontaminating methods may be satisfactory, each method has defects making it unsuitable for practical use.

The present invention provides a method of removing radioactive contaminants from a material, especially a foodstuff or water, comprising contacting said material with a phytin compound as adsorbent, said contacting taking place in a solution or suspension machine, agitating the mixture so formed and separating said phytin compound from said material.

The method has many advantages for example:

1. The method can be carried out without need of any additional equipment in an ordinary milk plant.
2. The method does not require any adjusting of the pH before and after treatment.
3. The method is simple in operation.
4. The composition and taste of cow's milk are not changed by the treatment.
5. The method is not expensive.
6. The method is not limited to use with cow's milk but can be applied to liquid food stuffs, drinks, and water used in processing foodstuffs.
7. The adsorbent to be employed occurs in nature, is readily available and its solubility is very low in water.
8. The method can be employed for domestic use.
9. The method is very efficient; that is, it treats a relatively large quantity per unit time and it leaves little or no contamination.
10. The adsorbent to be employed is nontoxic.

It has been found that phytin compounds extracted from rice bran can be used successfully in the method of the invention without any defects inherent in the conventional methods.

Phytin compounds suitable for use include Na-phytin [$C_6H_6O_{24}P_6CaMg_4Na_2 . 5H_2O$, molecular weight 921.33, purity 95.5], Ca-phytin [$_6H_6O_{24}P_6Ca_n . 5H_2O$, molecular weight 978.43, purity 93.1], Ca_4Na_2-phytin [$C_6H_8O_{24}P_6Ca_4Na_2 . 5H_2O$], and Ca_3Na_2-phytin [$C_6H_{10}O_{24}P_6Ca_3Na_2 . 5H_2O$], etc. The present inventor tested the effectiveness of these compounds in removing strontium 90 from cow's milk. The results are shown in Table 1.

TABLE 1

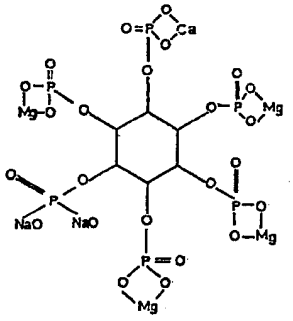
Removal of strontium 90 from cow's milk using various phytin compounds

Stirring time, min.	Na-phytin	Ca-phytin	Ca_4Na_2-phytin	Ca_3Na_2-phytin
5	77.1%	57.0%	65.0%	65.9%
10	79.8	65.1	67.1	68.6
20	81.4	66.3	67.6	70.9
30	83.5	69.6	70.2	72.0
60	88.0	70.1	72.3	75.2

Remarks: The pH of the cow's milk tested was 6.7 which was not adjusted. 80g of phytin compound was added to 1 l of cow's milk, after heating the mixture to 60 °C, stirred, cooled, and centrifuged.

Table 1 shows that phytin compounds are effective in removal of strontium 90, Na-phytin being especially effective.

The structure of the Na-phytin employed in the present invention is as follows:



Structural Formula of Na-Phytin

The solubility of Na-phytin at each pH is shown in Table 2.

TABLE 2

The amount of dissolved Na-phytin (mg/100ml buffer solution)

Temperature \ pH	pH5	pH7	pH9
1	407.02	57.03	20.12
20	415.97	51.44	20.12
40	278.43	48.64	21.25
60	203.51	38.02	23.37
80	145.37	33.55	29.07
97	114.06	28.29	33.10

NOTE: pH 5 (0.1 mole $CH_3COONa-CH_3COOH$ buffer)

pH 7 (0.1 mole CH_3COONa buffer)

pH 9 (0.1 mole $NH_4Cl—NH_4OH$ buffer)

On the other hand, the use of phytic acid in sequestering metals is well known, and phytic acid is used for removing metals such as calcium, iron, copper, etc. from brandy, wine, whisky, fruit wine, vinegar, sake, etc. However, phytic acid has not been heretofore used to remove radioactive contaminants from drinking water, water used in processing foodstuffs, or with foodstuffs other than the above mentioned. In particular, phytic acid has never been used for the purpose of removing radioactive materials from cow's milk. To maintain the quality of foodstuffs, particularly cow's milk, it is not desirable to adjust the pH and ash content in the course of treating the product. The present inventor has confirmed that the pH, ash content, and nitrogen content of cow's milk is not seriously changed by Na-phytin treatment. Especially the treatment does not impart any undesirable taste. (Refer Tables 3, 4, 5 and 6).

TABLE 3

Changes in cow's milk composition by the treatment of removing radioactive substances (Loss of the components and change of pH before and after treatment)

		Nitrogen	Calcium	pH
The method of the present invention	60°C	4.0%	0.3%	6.7 → 7.0
	5°C	0.3%	0.3%	6.7 → 6.9
The conventional method	70°C	23%	46%	82. → 5.4 → 8.2

NOTE: In the present invention 80g of Na-phytin was added to 1 l of cow's milk and was stirred at 5°C and 60°C for 10 minutes.

In the conventional method, 80g of calcium phosphate was added to 1 l of cow's milk, the pH of which had been adjusted to 5.4, and was stirred at 70°C for 10 minutes, and, thereafter, the pH was adjusted to 8.2.

In carrying out decontamination treatment of strontium 90 according to the method of the present invention, it was found that the percentage of radioactive substances removed varies depending upon the length of stirring time after the addition of the adsorbent, the temperature of the liquid on adding the adsorbent, the amount of adsorbent and, in centrifuging, the centrifugal force and time. The effect of the stirring time after adding the adsorbent, the liquid temperature on adding the adsorbent, the amount of adsorbent, and the pH of liquid on adding the adsorbent to the removing percentage of strontium 90 were determined in the method of the present invention. The results obtained in the case of using Na-phytin to remove strontium 90 from drinking water, an apple juice and cow's milk are shown in tables 4 to 6.

TABLE 4

Removing ratio of Strontium 90 from drinking water (%)

pH	5.0				7.0						9.0			
Temperature (°C)	25		60		25			60			25		60	
Quantity (g/l)	40	10	40	10	40	20	10	40	20	10	40	10	40	10
Taste and stirring time (minute)														
5	81.8	75.1	81.9	77.0	94.8	93.5	90.1	98.3	96.2	91.6	99.5	88.2	99.4	92.0
Taste	good	good	good	good	good	good	good	good	good	good	good	good	good	good
10	82.4	76.3	83.5	79.0	95.2	93.5	92.1	98.8	97.0	92.5	99.7	89.7	99.5	93.3
Taste	good	good	good	good	good	good	good	good	good	good	good	good	good	good
20	82.9	76.3	85.8	79.5	95.6	94.2	93.2	98.6	97.0	92.8	99.6	92.0	99.5	93.6
Taste	good	good	good	good	good	good	good	good	good	good	good	good	good	good
30	83.7	77.9	86.9	79.9	95.7		94.5		97.1	93.0	99.6	92.1	99.5	93.8
Taste	good	good	good	good	good		good		good	good	good	good	good	good

TABLE 5

Removing ratio of Strontium 90 from apple juice (%)

pH / Temperature (°C) / Quantity (g/l) / Taste and stirring time (minute)	3.4			
	25		60	
	20	40	20	40
5	72.1	87.1	76.1	89.5
Taste	good	good	good	good
10	76.8	89.5	81.8	92.9
Taste	good	good	good	good
20	97.7	91.1	85.3	94.1
Taste	good	good	good	good
30	81.1	/	86.1	94.6
Taste	good		good	good

TABLE 6

Removing ratio of Strontinum 90 from cow's milk (%)

pH	5.5	6.7						9.0			
Temperature (°C)	60	5		25		60		25		60	
Taste and Quantity (g/l) stirring time (minute)	80	80	40	80	40	80	40	80	40	80	40
5	60.1	59.7	51.3	61.4	52.9	77.1	49.8	53.3	47.8	49.1	36.3
Taste	good	good	good	good	good	good	good	good	good	good	good
10	63.4	62.9	53.9	62.2	59.7	79.8	52.9	54.1	49.6	55.0	41.7
Taste	good	good	good	good	good	good	good	good	good	good	good
20	65.9	65.1	55.2	63.7	59.6	81.4	52.7	54.5	50.8	59.2	42.7
Taste	good	good	good	good	good	good	good	good	good	good	good
30	68.0	68.5	55.7	65.5	61.9	83.5	53.2	57.9	52.3	61.7	43.8
Taste	good	good	good	good	good	good	good	good	good	good	good
60	71.9	69.9	55.8	70.5	64.3	88.0	61.0	60.8	54.9	63.3	50.1
Taste	good	good	good	good	good	good	good	good	good	good	good

NOTE: 1. In tables 4 and 6, a 10-person test panel compared the taste of items treated by the method of the present invention with the taste of untreated items. More than 7 out of 10 persons recognized no difference in taste between the two and both were indicated as "good".

NOTE: 2. In the experiment in Tables 4 to 6, the increase in pH of the liquid after treatment was within 0.3.

NOTE: 3. In the experiment in Tables 4 and 5, Na-phytin previously treated with phosphoric acid was used to prevent any increase in pH of the liquid to be treated.

The above-described result indicates that the following factors and conditions are preferable in attaining the object of the present invention:

1. A phytin compound is effective as an adsorbent, and, particularly, Na-phytin gives good results.

2. After addition of the adsorbent, it is preferable to stir more than 10 minutes, and, particularly, 20 to 60 minutes.

3. It is preferable to maintain the temperature of the liquid at 5 to 60°C, and, particularly, at 40 to 60°C.

4. The preferred amount of adsorbent per 1 of the liquid is 10 to 80g, and, particularly, 50—80g is effective.

5. The pH of the liquid to be added to the adsorbent is preferably 3.0 to 9.0, and 6.5 to 9.0 is particularly effective.

6. Although the adsorbent can be separated by settling, centrifugal separation at 400 to 1000 g (gravity) for 5 minutes is effective to shorten the treating time. And also a clarifier commonly used in the treating of cow's milk is applicable.

The method of the present invention can be applied in the treating of liquid foodstuffs, drinking water, and various foodstuffs. It is particularly effective in the treating of cow's milk because cow's milk is usually stored in a milk storage tank before processing, and while it is in storage the adsorbent can be added to the milk. The mixture is stirred, and thereafter clarified to separate the adsorbent from the milk. For example, when Na-phytin was added to cow's milk in a milk storage tank (the milk temperature was about 5°C and the amount of Na-phytin added was 80g per 1 l of milk), and was stirred for 30 minutes, the percentage of radioactive contaminant removed was 70%. Further, if the milk temperature is 40 to 60°C and the adsorbent is removed by centrifugation, more than 80% of the radioactive contaminant is removed. This can be explained by the fact that the solubility of Na-phytin decreases as the temperature increases. But the remarkable feature of the present invention is that Na-phytin compounds are semipermanent and can be utilized without regenerating or scraping the compound once used as in the prior methods. As one example, the operation of removing strontium 90 from cow's milk with Na-phytin was repeated 10 times using the same Na-phytin. The results are shown in Table 7.

TABLE 7

Percentage of Strontium 90 removed from cow's milk without changing or recharging the Na-phytin

Trial Exper. No.	1	2	3	4	5	6	7	8	9	10
Percentage removed	88.0	82.1	80.7	76.6	75.9	75.2	74.3	74.5	74.6	74.2

Remarks: 80g of Na-phytin was added to 1 l of cow's milk of pH 6.7 and the mixture was stirred at 60°C for 60 minutes and centrifuged.

Thus, according to the method of the present invention it is possible to use the same adsorbent repeatedly without regeneration and therefore the treatment cost is reduced remarkably.

The method of the present invention can be applied not only to drinking water, liquid foodstuffs and cow's milk, but also the steps of treating and processing various foodstuffs contaminated with radioactive substances. For example, in manufacturing sugar from cane contaminated with a radioactive substance, the radioactive substance can be removed by adding phytin compound to the sugar juice pressed out by the conventional method and using the phytin compound to eliminate the radioactive substance. The results of experiment to attest the effects of pH, temperature of sugar juice and the amount of added Na-phytin on the removal of strontium 90 thereof are shown in Table 8.

TABLE 8

Removing ratio of Strontium 90 from sugar juice (%)

pH	7.0						9.0			
Temp. (°C)	40			60			40		60	
Quantity (g/l)	40	20	10	40	20	10	40	10	40	10
Stirring time (minute)										
5	83.4	66.3	45.7	92.6	82.4	68.6	93.4	61.1	95.8	82.1
10	84.2	70.2	49.8	95.0	87.7	75.1	95.3	63.9	97.7	85.0
20	85.0	72.2	54.8	95.8	90.8	82.0	95.9	67.7	97.6	86.2
30	88.8	75.7	57.5	97.1	92.6	83.9	95.8	69.2	98.3	86.9

On the other hand, in the household, too, the method of the present invention can be applied to the raw foodstuffs contaminated with a radioactive substance. For example, when cooking an instant soup contaminated with a radioactive substance the radioactive substance can be easily removed by, after dissolving the instant soup in water or hot water, by adding a phytin compound thereto, stirring, and filtering through a cloth with small mesh. And also, when washing vegetables and fruits contaminated with radioactive substances, the radioactive substances adhering on the surfaces of vegetables and fruits can be easily removed by washing them with water to which a detergent and a phytin compound have been added. Thus, the method of the present invention is a novel method which has various applications over a wide area, and is very advantageous in the points that the operation of removing radioactive substances is very simple and remarkably little time, cost, and labor is required for the treatment.

EXAMPLE 1

10 Kg of Na-phytin (pretreated with phosphoric acid to prevent variation in pH) was added to 1000 l of city water or water used in processing foodstuffs containing strontium 90 and, after stirring at the ordinary temperature for 30 minutes, the Na-phytin having adsorbed strontium 90 was removed by centrifugation. By this operation 94.9% of the strontium 90 in the drinking water or water for processing foodstuffs was removed. The pH of the water so obtained was not changed and the taste was not vitiated.

EXAMPLE 2

2 Kg of Na-phytin was added to 100 l of sugar juice pressed out from cane by the conventional method and, was stirred, heated to 60°C, and, after adjusting the pH to 7.0 by adding 30g of lime, allowed to stand overnight. By this operation, 90% of the strontium 90 in the supernatant was removed. The product obtained by this treatment was not unusual in taste, appearance and composition in comparison with the conventional product.

EXAMPLE 3

8 Kg of Na-phytin was added to 100 l of cow's milk (pH 6.7) containing strontium 90, and, after stirring at 5°C for 1 hour, was heated to 60°C, and the Na-phytin, having adsorbed strontium 90, was separated by centrifugation. By this operation, 80.1% of the strontium 90 contained in the cow's milk was removed. The cow's milk so treated had pH of 6.7; the pH did not vary throughout the treatment and the treated product had a good palatability.

WHAT I CLAIM IS:—

1. A method of removing radioactive contaminants from a material comprising contacting said material with a phytin compound said contacting taking place in a solution or suspension medium as an adsorbent, agitating the mixture so formed and separating said phytin compound from said material.

2. A method as claimed in claim 1 in which the agitating is effected by a stirring action.

3. A method as claimed in claim 2 in which the mixture is stirred for more than 10 minutes after the material has been contacted by the phytin compound.

4. A method as claimed in claim 3 in which the mixture is stirred for from 20 to 60 minutes after the material has been contacted by the phytin compound.

5. A method as claimed in any of claims 1 to 4 in which 10 to 80 g. of phytin compounds is present per litre of liquid.

6. A method as claimed in claim 5 in which 50 to 80g of phytin compound is present per litre of liquid.

7. A method as claimed in any of claims 1 to 6 in which the liquid has a pH of from 3 to 9.

8. A method as claimed in claim 7 in which the pH is from 6.5 to 9.

9. A method as claimed in any of claims 1 to 8 in which the separation is effected by settling or centrifuging.

10. A method as claimed in claim 9 in which centrifugal separation is effected using a force of from 400 to 1000g.

11. A method of removing radioactive contaminants from foodstuffs or water comprising adding a phytin compound as an adsorbent thereto, and, after stirring, separating said phytin compound.

12. A method of removing strontium 90 from cow's milk contaminated therewith comprising adding Na-phytin to said cow's milk, and, after stirring, centrifuging said cow's milk at a temperature of from 40 to 60°C. in order to effect separation of said Na-phytin adsorbent.

13. A method of removing strontium 90 from the surface of vegetables or fruits contaminated therewith comprising washing said vegetables or fruits with water containing a detergent together with a phytin compound.

14. A method of removing radioactive contaminats from raw substances to obtain an uncontaminated product comprising adding phytin compound in a processing step agitating the mixture so formed and separating said phytin compound from said mixture.

15. A method as claimed in any of claims 1 to 14 wherein the radio-active substance is strontium 90.

16. A method as claimed in any of claims 1 to 15 wherein the phytin compound is Na-phytin.

17. A method as claimed in any of claims 1 to 15 wherein the phytin compound is Ca-phytin.

18. A method as claimed in any of claims 1 to 15 wherein the phytin compound is Ca_4Na_2-phytin.

19. A method as claimed in any of claims 1 to 15 wherein the phytin compound is Ca_3Na_2-phytin.

20. A method as claimed in claim 1 substantially as hereinbefore particularly described with reference to any of the foregoing Examples.

W. P. THOMPSON & CO.,
12 Church Street, Liverpool, 1
Chartered Patent Agents.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1970.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.